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AND PROPERTIES

WORKING PARTY ON STRUCTURE AND PROPERTIES OF COMMERCIAL POLYMERS*

RELATIONSHIP BETWEEN MOLECULAR CHARACTERISTICS AND PHYSICAL PROPERTIES OF LINEAR LOW DENSITY POLYETHYLENES

Prepared for publication by

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Relationship between molecular characteristics and physical properties of linear low density polyethylenes

Abstract - The relationship between molecular characteristics and physical properties of linear low density polyethylenes (LLDPE) was investigated in comparison with low density polyethylenes produced by high pressure processes (HP-LDPE). Differences in molecular characteristics, such as branching structure, spherulite structure and solution properties between LLDPE and HP-LDPE were made clear. A comparison of both polymer films in an impact strength and heat resistance was made. The higher Vicat softening point of LLDPE compared with HP-LDPE could be attributed to the thicker lamella of LLDPE than that of HP-LDPE because of the difference of the branching structures. Some comparisons of LLDPE with HP-LDPE on rheological properties and processability parameters were tried. There are apparent differences between both polymers in the dynamic viscoelastic properties and the extensional viscosity development. The melt flow rate value, which is widely used as a processability parameter, of LLDPE is more than one decade lower than that of HP-LDPE at a given molecular weight because of the difference of the molecular dimension. The melt tension, which is another processability parameter widely used, of LLDPE is lower than that of HP-LDPE at a given melt flow rate. The melt tension data also suggest that the melt tensional properties and processability are mostly governed by a nonlinear extentional properties of the melts in a long time scale.

INTRODUCTION

The manufacturing method of low density polyethylenes by radical polymerization under conditions of the tamperature and pressure (200 ~ 200°C, 1000 ~ 3000 Kg/m²) was found by Imperial Chemical Industries in 1933. Later on, a new method for namufacturing low density polyethylenes by copolymerization of ethylene and co-leftins with Ziegler catalysts (T-catalyst systems) or Phillips catalysts (Cr-catalyst systems) under moderate conditions of temperature and pressure (60 ~ 200°C, 5 ~ 200Kg/m²) was developed. This method for manufacturing linear low density polyethylenes (LDDR) by copolymerization of ethylene and c-cloffins subsided the substance of the substance o

Although LLDPE thus developed has been replacing high pressure low density polyethylenes (MP-LDPE) in various fields of the market, quite a few academic reports on structures and/or properties of LLDPE commercially manufactured have been published (ref. 1,2). The Sub-Croup meeting in Japan of IURA (Morking Patry 1N-2-1 has worked to investigate the relationship between molecular characteristics and physical properties of commercially manufactured LLDPE results of the experiments and discussions which have been made by the Sub-Croup for these vowers. Moscular characteristics of LLDPE are given in the third backcroup in the forth and fifth sections, mechanical and thermal properties and rheological properties of LLDPE are given in the third in the forth and fifth sections, mechanical and thermal properties and rheological properties of LLDPE studies incorporately we believe that these studies incorporated herein would be very useful for the accurate understanding of the qualities of LLDPE which will be more preventent in the future.

MATERIALS

Linear low density polyethylenes (LLDPE) employed in this report are commercially available

ones which were manufactured by solution polymerization processes of Mitsui Petrochemical (Nee-zex, Ultrax) and Dox Chemical (Dovleys). Other types of polyetylenes (HDPS, HP-LDPS), polybutene-l and polyoctene-l were also used for comparisons. These polymers were commercially manufactured except polyoctene-l which was prepared in the laboratory scale. The weight-average molecular weights M_w, the molecular weight distributions M_w/M_n, the densities and the manufactures (trade names) are qiven in Table 1.

TENTE 1	Mologular	characteristics	of polymora	own lowed

Resin	м _w ж 10 ч	M _W /M _n	d g/cm ³	Resin manufacturer (Trade name)
HDPE	5 ∿ 15	5 ∿ 7	0.955 ∿ 0.968	Mitsui Petrochemical (Hi-zex)
LLDPE	5 ∿ 20	3 ∿ 7	0.920 ∿ 0.945	Mitsui Petrochemical (Neo-zex, Ultzex) Dow Chemical (Dowlex)
HP-LDPE	18 ∿ 31	6 ∿ 10	0.920 ~ 0.929	Mitsui Polychemical (Mirason)
Polybutene-1	100	7	0.915	Shell Chemical (Shell Polybuthylene)
Polyoctene-1	10	6		(experimental resin)

The Sub-Group IV-2-1-2 (Eastern Europe, Chairman: Dr.Stejskal) kindly cooperated in determining M_o of our LLDPE samples (3 samples) by a light scattering method. Unfortunately, there was difference between their data measured in diphenylmethane solutions and ours in 1-chloronaphthalene. Accordingly, we could not adopt their data in this report to our regret.

CHARACTERISTIC STRUCTURES AND PROPERTIES OF LINEAR LOW DENSITY POLYETHYLENES

LLDPE is different from HP-LDPE in the molecular structure, such as branching structure, molecular weight distribution and chemical composition distribution, and also in higher order structure, such as crystalline/amorphous structure and spherulite structure. In this section, the characteristic structures and the solution properties of LLDPE are described in comparision with HP-LDPE and a few other polyclefins.

Branching structure and density

NB-LOPE manufactured by conventional radical polymerization has long-chain branchings mainly. On the other hand, LLDPE is a linear polymer with short-chain branchings originated from c-lefin used as a comcomer. Figure 1 shows that the density of LLDPE decreases as the comcomer content in a chain increases. The density of ethylene/d-enthylenenced copolymer loopolymer decreases some rapidly with the comcomer content than ethylene/butene-l copolymer lattice, while butene-l is easily incorporated into the crystal lattice (ref. 3).

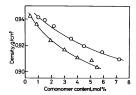


Fig. 1. Density vs. comnomer content correlation for LLDPE: Open circles and triangles denote for the values for ethylene/butene-loopolymers and ethylene/4-methylpentene-loopolymers, respectively.

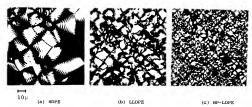


Fig. 2. Spherulite structures of polyethylenes: (a);d=0.968, (b);d=0.920 (c);d=0.929

Spherulite structure

Figure 2 shows spherulite structures of HDPE, LLDPE and HP-LDPE. The differences among them are fairly clear. HDPE has the well-grown spherulite structure. On the other hand, LLDPE has the small and indistinct spherulite structure because the short-chain branchings hinder the crystallization and the formation of spherulite. This is more remarkable in the case of HP-LDPE having long-chain branchings. These facts shows that the shape and size of spherulites of the polyethylenes are strongly dependent on the length and frequency of branching in the molecules.

Solution property

The whole polymers of HDPE, LLDPE and HP-LDPE were fractionated by a column fractionation method. Then, the weight-average molecular weights Mw of the fractions were measured by a light scattering method in 1-chloronaphthalene at 135°C. The intrinsic viscosities [n] were measured in decalin at 135°C. Relations between Mw and [n] for different series of polyethylenes are shown in Fig. 3. [n] of LLDPE is almost equal to that of HDPE at a same Mw, but higher than that of HP-LDPE. This result well corresponds to that obtained through the comparison between HDPE and HP-LDPE by Trementozzi (ref. 4). The result shown in Fig. 3 suggests that the molecular dimension in decalin solution for HP-LDPE having long-chain branchings is smaller than that for linear polyethylenes of the same Mw. In the case of HP-LDPE, the higher the molecular weight becomes, the more easily the long-chain branchings are formed because of the increasing opportunity of chain transfer from polymer radicals to polymer chains during polymerization. This is the reason why the slope of [n] vs. My curve for HP-LDPE decreases in the high Mw region as is seen in Fig. 3 : Molecular dimension of polymer chain having many long brnchings is much smaller than that of linear counterpart with the same molecular weight. The schematic representations of LLDPE and HP-LDPE chains in good solvent are illustrated in Fig. 4.

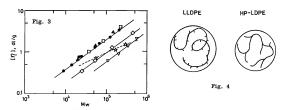


Fig. 3. Intrinsic viacosity [n] wa. weight-average molecular weight M_p correlation for fractionated polymers: [].HBME(d-0.900, Φp-thylend-p) butene-1 copolymer (4-0.935), Δiethylene/cotene-1 copolymer (4-0.939), Δy-thylene-1 copolymer (4-0.9

Fig. 4. Schematic representations of LLDPE and HP-LDPE chains in good solvent.

Figure 3 also shows the relations between N_w and [n] for fractions of polybutene-1 and polyoctene-1, in which ethyl and heavy heranchings are altermately connected to carbons of main chains, respectively. Two straight lines drawn on the [n] date for both polymers are parallel to those for miDrs and LLDPFs. [n] values for the series of linear polyolefins seems to depend on the length of main chain. In Fig. 5, [n] values of the four series of polyolefins (IDRFs, polybutene-1 and polyoctene-1) are plotted against the weight—average molecular weights of main chains N_w. For polybutene-1 and polyoctene-1, N_w=(1/2)N_w, and (1/4)N_w, respectively. It is apparent from this figure that linear polyolefins with the same main chain length have approximately the same molecular dimension in good solvent, recardless of length of short-chain branchings. Taking a cood look at the figure, the data points for polybutene-1 and polyoctene-1 are located a little lower than those for the linear polyethenes. The reasonable explanation for this difference has not come out yet.

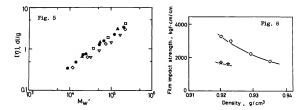


Fig. 5. Intrinsic viscosity $[\eta]$ vs. weight-average molecular weight of main chain M_{ϕ} , correlation for fractionated polymers. Symbols are the same as in Fig. 3.

Fig. 6. Impact strength vs. density correlation for LLDPE and HP-LDPE films: Open circles and stars denote the values for LLDPE (MFR=2V3) and HP-LDPE (MFR=2V3), respectively. Tubular films were tested at room temporature.

MECHANICAL AND THERMAL PROPERTIES OF LINEAR LOW DENSITY POLYETHYLENE FILMS

As was seen in the preceeding section, molecular characteristics of LLDPR are different from those of HP-LDPE in spite of similar density of both polyethylenes. Accordingly, it is very important that the physical properties of both polyears of the same density are compared with each other and differences are made clear. In this section, such a comparision of both polymer films in an impact strength and heat resistance have been made.

Impact strength

One of the physical properties of LLDPE film superior to that of HP-LDPE film is the extremely high impact strength. The film impact strengths of LLDPE and HP-LDPE measured by the film impact tester (Toyosekić Co.) at room temperature are plotted against the density in Fig. 6. Tested samples are 30 pm thick and of similar melt flow rate (MFR). As is shown in this figure, LLDPE film gives about two times higher impact strength than HP-LDPE film at the same density.

As a major factor to improve the impact strength, the existence of impact relieving portion is conceivable. The storage modulus E' and loss modulus E' of two LURPS and HP-IDPE were measured by Rheovibron-II at 110Hz. No difference in the viscoclastic properties was recomized amono them as shown in Fig. 7. Then, eletron microscopic investigation of the fracture portions of polyethylene films at roos temperature revealed that ductile fractures developed mainly. In fact, Fig. 8 which exhibits the result of high speed tensile test (tensile speed is 1000mm/min), clearly shows the much higher tensile strength and elongation for LLDPE film than for HP-IDPE film.

Considering this experimental results from the view point of higher order structure, there presumably exist more tie molecules connecting the lamella of LLDPE having long main chain than BP-LDPE having short main chain due to long-chain branchings. Consequently, LLDPE shows the higher toughness (the total energy absorbed to the break point) and the higher impact strength than BP-LDPE.

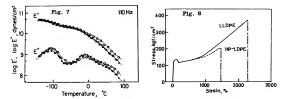


Fig. 7. Storage modulus (E') and loss modulus (E") of polyechylenes as a function of temperature at 110Hz. Open circles, triangles and closed circles denote the values for chiplene/butene-l copolymer(deo.935, MFR-1.6), ethylene/a-ethylene/a-ethylene/a-ethylene/a-ethylene/a-ethylene/butene-l copolymer(deo.930, MFRe-2.1) and HP-LDPE(deo.921, MFRe-2.9), respectively. E' and E" were measured by Rheoviknor-II.

Fig. 8. Stress-strain curves for LLDPE(d=0.920, MFR=2.1) and HP-LDPE(d=0.921, MFR=2.9). Tensile speed is 1000mm/min.

Heat resistance

As a yard-stick for judging the use-limitation at high temperatures, the Vicat softening point is generally used. As is understood from Fig. 9, LLDWE has the Vicat softing point about 10°C higher than HP-LDWE of the same density, usugesting that LLDWE is superior to HP-LDWE in terms of the heat resistance. The data for HDVE are located on the extension of those for LLDWE.

Figure 10 shows BSC selting behavior of LLDPE and HP-LDPE of almost the same density (600-300 and 0.021, respectively). HP-LDPE gives a broad pattern of matting with the peak at 107°C. On the other hand, LLDPE shows three peaks in the BSC malting endothern at 106, 119, 123°C. Considering the fact that each fraction of LLDPE by chemical composition shows a respective sincle peak, the overlaping pattern of DSC for LLDPE would be due to the chemical composition distribution.

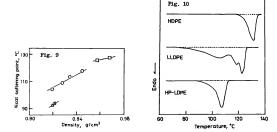


Fig. 9. Vicat softening point vs. density correlation for polyethylenes. Squares, open circles and stars denote the values for HDPE(MFR= 5/10), LDDPE(MFR=0.2*4) and HP-LDPE(MFR=2*03), respectively.

Fig. 10. DSC curves for polyethylenes: HDPE(MFR=5, d=0.968), LLDPE (MFR=2, d=0.920), HP-LDPE(MFR=3, d=0.921). Data were taken with DSC-II (Perkin-Elmer).

A good correlation between the melting point determined by DSC and the lamella thickness measured by a Raman spectrosopic method for HP-IDPS and fractionated LIDPS is shown in Fig. 11. In this figure, a (LIDPS) and b (HP-LIDPS) are of approximately the same density, i.e. 40-202 0-921. It is conceived that the lamella of HP-LIDPS can not cross thick due to the existence of the long-chain branchings. On the other hand, the thick lamella of LIDPS is resulted from that the Hinear structures affects positively the formation of perfect is resulted from that the Hinear structure affects positively the formation of perfect would be attributed to the thicker lamella of LIDPS than HP-LIDPS coulses of the difference of the branching structures.

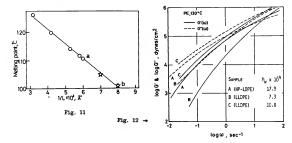


Fig. 11. Melting point vs. lamella thickness (L) correlation for HP-LDPE and fractionated LLDPE. Open circles and stars denotes LLDPE (d=0.940 $^{\circ}$ 0.921) and HP-LDPE (d=0.928 $^{\circ}$ 0.920), respectively.

Fig. 12. Frequency dependences of dynamic storage modulus G'(ω) and loss modulus G'(ω) for a HP-LDPE sample (A) and two LLDPE samples (B and C) at 130°C. The weight-average molecular weights of the samples are indicated in the floure.

RHEOLOGICAL PROPERTIES AND PROCESSABILITY OF LINEAR LOW DENSITY POLYETHYLENES

The processability of polymeric materials is closely related to the rheological properties in the molten state. As is well known, for example, the bubble stability in the fills blowing process of LLDPE is much inferior to that of HP-LDPE with a similar melt flow index. This mutableness often makes problems in processing of the commercial polymers. But the reason has not fully understood yet. Accordingly, it is significant to investigate the rheological properties of LLDPE in the molten state and the processability of the same material.

In the present section, some comparisons of LLDF2 with HP-LDF2 on various rheelogical properties and processability parameters are tried and the origin of the difference in processability between the two types of commercial polyethylenes is discussed in terms of the rheological properties. For better comparisons, the three particular samples, one of HP-LDF2 (A) and two of LLDF2 (B and C) were picked up from various samples shown in Table 1. The weight-average molecular weights M, measured in 1-ohloromaphthalene at 135°C, and the intrinsic viscosities [n] measured in decalin solutions at 135°C and the molecular weight distribution M,M,M for the sample A, B and C are as follows.

A (HP-LDPE):
$$M_{W} = 1.79 \times 10^{5}$$
, $[\eta] = 1.07 \text{ d1/g}$, $M_{W}/M_{\Pi} = 6.4$
B (LLDPE): $M_{W} = 7.3 \times 10^{4}$, $[\eta] = 1.50 \text{ d1/g}$, $M_{W}/M_{\Pi} = 4.5$
C (LLDPE): $M_{W} = 1.08 \times 10^{5}$, $[\eta] = 1.86 \text{ d1/g}$, $M_{W}/M_{\Pi} = 7.0$

Dynamic viscoelastic properties

The frequency dependences of the dynamic linear viscoelastic functions, the storage shear modulus C*(0,0) and loss modulus C*(0,0) of HP-LDPE (0,) and LLDPE (8 and C) measured with a Rheometrics Mechanical Spectrometer are shown in Fig. 12. The weight-average molecular weights for the samples are shown in the figure.

The frequency dependence curves of LIDPE melts are clearly different from those of HP-LDPE in the shapes 19th G' and G' curves for LLDPE are most ateaper than those for HP-LDPE. This suggests that the distribution of relaxation times is broader in HP-LDPE as compared with that in LDPE. It is well known that the broader molecular weight distribution (ref. 5) and branching of the polymer chain (ref. 6,7) make the distribution of relaxation times associated with the entanglement slipping in the polymeric liquids be broad. On account of the polymer chain the property of the p

Extensional viscosity development

In connection with the polymer processing, especially with film blowing and blow moulding processes, the extensional properties of materials in the molten state are undoubtedly important. The extensional viscosity development curves for the three samples are shown in Fig. 14. The extensional viscosity development ogit as a function of time after applying a constant rate of strain t was measured with Maissner-type (ref. 8) of apparatus. Then the constant rate of strain t was measured with Maissner-type (ref. 8) of apparatus. Then the constant is a state of strain t was measured at the materials. The experimental results measured at three rates of strain (I, II and III) for each sample (A, B or C) are drawn as illustrated in the figure.

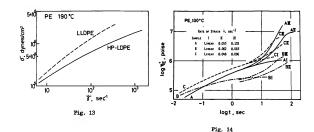


Fig. 13. Shearing stress σ and rate of shear $\dot{\gamma}$ relations for typical samples of LLDPE and HP-LDPE at 190°C.

Fig. 14. Extensional viscosity (η_E^+) development curves for a HP-LDPE (A) and two LLDPE (B and C) at 130 $^{\circ}C.$

The "Linear" curves in the figure (I) were calculated from the linear vicoelastic functions G' and G'' shown in Fig. 12 and correspond to $\eta_R^+(t)$ when $\dot{\epsilon} + 0$.

The might find the deshibits an up-turn deviation from the "Linear" line in long time region and the becomes more remarkable with increasing &. The curves for LIDDE samples (B and C) are similar in the shapes but different in the values; the sample C having higher molecular using the content of the property of the pr

Melt flow rate
The melt flow rate or melt flow index has been widely used as a common measure for judging the processability of commercial thermoplastic materials. In Fig. 15, the molecular weight dependence of melt flow rate, MFR, for LLDPE are compared with that for HP-LDPE. The MFR was measured under the weight of 2kg at 190°C according to ASTM D1238E. Among the data points for various samples given in Table 1, those of the particular samples A, B and C used for the measurement of rheological properties shown in Fig. 12 and 14 are marked by the sample codes.

The slope of the straight lines is -2.9, suggesting that MFR is proportional to $M_{\omega}^{-2.9}$ for both materials. This power index 2.9 is a little lower than 3.5, the well known number for the molecular weight dependence of viscosity. The lower dependence is, of course, due to that MFR is a flow rate at fixed shearing stress in the non-Newtonian flow regime. As is

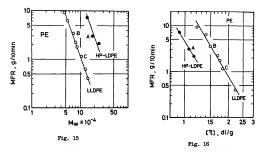


Fig. 15. Melt flow rate, MFR, plotted against weight-average molecular weight Mw for HP-LDPE and LLDPE. A, B and C correspond to the samples used in Figs. 12 and 14.

Pig. 16. Melt flow rate, MFR, plotted against intrinsic viscosity [η] for HP-LDPE and LLDPE. A. B and C correspond to the samples used in Pigs. 12 and 14.

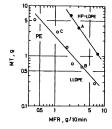
seen from this figure, MFR value of LLDPE is more than one decade lower than that of HP-LDPE at a same molecular weight; the viscosity of LLDPE is higher than that of corresponding HP-LDPE. These difference is clearly due to the fact that the molecular dimension of LLDPE is larger than that of HP-LDPE as discussed in the previous section (Solution property) and also illustrated in Fig. 4.

MFR values of the same samples as those in Fig. 15 are plotted against the intrinsic viscosity [n] in Fig. 16. The zero-shear viscosities no of branched polymer melts and the linear counterparts have been found to be successfully expressed (ref. 6,7,9-12) by a unique line when those are plotted against the molecular dimension and/or intrinsic viscosity.

In the case of the polyethylenes studied in this report, however, the data for HP-LDPE did not fall on the line for LLDPE as can be seen in Fig. 16. The reason would be that the LLDPE is not exactly the counterpart of the branched low density polyethylene.

Melt tension

Besides the melt flow rate, the melt tension, MT, has also widely used for the evaluation of processability of commercial polymers. The MT becomes more significant in the case that the extensional deformation and elastic properties play a important role in polymer processing such as film blowing and blow moulding. The MT data are plotted against the MFR for LLDFE and HP-LDPE samples in Fig. 17. The MT was measured under the conditions; the extrusion speed of 10mm/min, take-up speed of 12.6m/min and the die diameter of 2.1mm. Both series of polyethylene samples make the respective linear relations between log MT and log MFR. At a



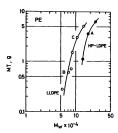


Fig. 17. Melt tension MT plotted against melt flow rate MPR for HP-LDPE and LLDPE. A, B and C correspond to the samples used in Figs. 12 and 14.

Fig. 18. Melt tension MT plotted against weight-average molecular weight M. for HP-LDPE and LLDPE. A, B and C correspond to the samples used in Figs. 12 and 14.

same value of MFR. MT of HP-LDPE is higher than that of LLDPE, suggesting that the bubble stability of film blowing process is worse for LLDPE as compared with that for HP-LDPE. It is also interesting that the order of MT values of the samples A, B and C indicated in this figure is exactly the same as that of the extensional viscosities in long-time region at finite rates of strain (II and III) as shown in Fig. 14. This fact suggests that the melt tensional properties and processability in film blowing are mostly governed by a nonlinear (at high rates of strain) extensional properties of the melts in a long time scale.

Figure 18 shows the molecular weight dependences of MT for the two series of polyethylenes. The MT strongly depends on molecular weight and the values of LLDPE is higher than that of HP-LDPE at a same Mw, but not at same MFR as was shown in Fig. 17. It can finally be concluded that a high MFR (= a low viscosity at low rates of shear) and a high MT (= a high nonlinear extensional viscosity at long times) are necessarily required to attain a better processability of polyethylenes. These somewhat contradictory requirements would be satisfied by making the linear chains be lightly crosslinked to give a branched molecules or by blending a small amount of long branched polymer to the linear polymer.

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